

PTO 06-1848

CY=JA DATE=19840315 KIND=A
PN=59-046125

MANUFACTURE OF MICROCAPSULE
[MAIKUROKAPUSERU NO SEIZOHO]

Tetuya Kimijima, et al.

* 103
Motivated to select
any gelant or gell-forming
agent of the genus of the
expectation that any member
of the gelling genus intended
success the

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C.

January 2006

Translated by: FLS, Inc.

genus
contains a gelatin
core is covered w/ hydrophobic polymer
particle size of 50 μ m
"freeze shattered"

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	59046125
DOCUMENT KIND	(12):	A
PUBLICATION DATE	(43):	19840315
PUBLICATION DATE	(45):	
APPLICATION NUMBER	(21):	57155539
APPLICATION DATE	(22):	19820907
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	B01J 13/02; //A23L 1/00; C09J 5/00
DOMESTIC CLASSIFICATION	(52):	
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTOR	(72):	KIMIJIMA, TETSUYA; SADA, TOMOHIKO; TANIGUCHI, MASAYUKI.
APPLICANT	(71):	NIPPON OXYGEN CO., LTD.
TITLE	(54):	MANUFACTURE OF MICROCAPSULE
FOREIGN TITLE	[54A]:	MAIKUROKAPUSERU NO SEIZOHO

Specifications

1. Title of the Invention

Manufacture of Microcapsule

2. Claim(s)

(1) Manufacture of a microcapsule characterized by freezing, grinding and powdering a core substance, which comprises a substance that becomes a liquid, agglomerates, or cannot keep its powdery form near room temperature, when obtained in powder form, at a low temperature at which the powder thereof does not thaw or agglomerate, then mixing and stirring this with a fine powder having a smaller particle size than this powder at a temperature near the above-mentioned low temperature.

(2) Manufacture of a microcapsule characterized by freezing, grinding and powdering a core substance, which comprises a substance that becomes a liquid, agglomerates, or cannot keep its powdery form near room temperature, when obtained in powder form, at a low temperature at which the powder thereof does not thaw or agglomerate, then mixing and stirring this with a fine powder having a smaller particle size than this powder at a temperature near the above-mentioned low temperature and subsequently covering it further with a polymer film.

Detailed Specifications

This invention relates to a method for microencapsulating a liquid, a substance having a tackiness or a soft substance especially near room temperature.

Microcapsules can be used widely in pressure-sensitive copy paper and also in medicines, agricultural chemicals, fragrances, etc.

There are methods, such as: 1. coacervation method. 2. interfacial polymerization method, 3. in situ polymerization method, 4. drying-in-liquid method, 5. thawing, dispersion and cooling method, 6. orifice method, 7. spray-drying method, 8. suspension-in-air covering method. 9. inorganic wall microencapsulating method, and the like for the manufacture of typical microcapsules in the past. However, by using such methods of manufacture, there are the following drawbacks when a liquid or a substance having tackiness or a soft substance, such as water, an organic solvent, starch syrup, paste, tacky adhesive or bonding agent is microencapsulated at room temperature. That is, while dispersing the core substances comprising the above-mentioned substances in a dispersion medium in methods 1 to 5, the core substance particles stick to each other and agglomerate when the core substance is tacky. Moreover, adjusting the wetting and specific gravity of the core substance and polymer solution is required, the work is troublesome, and moreover, the characteristics of the finished capsule are not satisfactory either. In addition, in the method 6, a capsule on the order of microns is difficult to make and the production efficiency also is poor. Furthermore, although the methods 5, 7 and 8 can be used for encapsulating toners, a uniform film thickness and completely covered capsule is difficult to make, and agglomeration is invited in the case of a substance stronger in tackiness than the toner. Moreover, since water or an organic solvent is used in the methods 1 to 8, a core substance

submerged in the water or organic solvent that reacts therein cannot be encapsulated, the organic solvent post-treatment is troublesome, drying is required to produce the capsule as a powder, and there is the danger of a fire or explosion. Furthermore, when the core substance is soft, in the method 9, a large amount of wall substance contaminates the interior of the core substance, and instead of a capsule, it readily becomes a mixture.

No microcapsules could be manufactured in a satisfactory state from a substance which becomes a liquid or agglomerates near room temperature in any of the methods 1 to 9, or when a powder form is obtained.

This invention was accomplished in view of the above-mentioned circumstances, and it is an object to provide the manufacture of a microcapsule wherein a liquid, a substance having tackiness, a soft substance, a substance submergible in or reacts with water or an organic solvent, or the like can be microencapsulated easily and safely at room temperature with high efficiency, without deteriorating or denaturing the above-mentioned substance.

This invention will now be described in detail.

A substance which becomes a liquid, agglomerates, or cannot keep its powdery form near room temperature (0°C to 50°C) when obtained in a powder form, such as an aqueous solution, aqueous dispersion, tacky adhesive, bonding agent, paint or organic solvent, can be used for the core substance used in the manufacture of this invention.

In addition, when the flowability of the resulting microcapsule needs

to be enhanced even more, or to more completely cover it with the wall substance, a small amount of a fine powder having an average particle size of about 100 μm or less can be added as follows. Fine plastic resins, such as fine silica powder, various bentonites, aluminum oxide, carbon black, calcium carbonate, talc, kaolin, magnesium carbonate, titanium oxide, zinc oxide, aluminum powder, fine ceramic powder, polyethylene, nylon and methacrylates; phytic acid and its metal salts, fine powders subjected to a surface treatment with starch or the above powders are cited for the fine powder, but one free of an affinity for the core substance is selected. In particular, when the core substance is a liquid having a viscosity of about 100 centipoise, a fine powder having affinity to it should be avoided unconditionally. That is, it is necessary to select a hydrophobic fine powder if the core substance is hydrophilic, and it is necessary to select a hydrophilic fine powder when the core substance is hydrophobic. Moreover, a fine powder whose particle size is smaller than the particle size of the powder obtained by freezing and grinding the core substance, and preferably, a fine powder having a particle size of one-tenth or less is used.

freeze shattered

The microencapsulation is described next. Firstly, the core substance is frozen using the coolness of liquid nitrogen or the like and powdered in this state. The temperature at this time varies depending on the type of core substance; it is about -20°C with an aqueous solution, aqueous dispersion, etc. It is about -30°C to -80°C with a tacky or readily-agglomerable substance, such as a tacky adhesive or bonding agent.

A powder having an average particle size of 1 to 1,000 μm is obtained by suitably adjusting the rotating speed (grinding speed) of the stirrer and the grinding temperature.

Then, by keeping this powder at a low temperature, the above-mentioned wall substance is added, mixed and stirred so that it does not agglomerate or thaw, to microencapsulate the powder. It is preferable to use a high-speed stirrer with a cutter provided with a liquid nitrogen cooling jacket. The stirring conditions include a stirring rate of 5,000 to 20,000 rpm and a stirring time of 1 to 10 minutes. In particular, when this type of stirrer is used, the above-mentioned freezing and grinding are performed in this device, which is advantageous from a processing standpoint. Otherwise, a ball mill, stirrer with a cutter, attriter, or the like also can be used for the mixing and stirring. The temperature during stirring is the same as the temperature during the above-mentioned freezing and grinding. In order to prevent the temperature from rising owing to frictional heat, it is necessary to continually cool the stirrer by way of a coolant, such as liquid nitrogen. Moreover, the mixing ratio of the core substance powder and the wall substance is affected by the shape of the core substance powder as well. Although this is completed with a small amount of fine powder when the powder is spherical, normally, the amount of the fine powder is 0.5 to 20 weight parts per 100 weight parts of the core substance powder. Furthermore, the particle size of the resulting microcapsule is determined by the particle size of the core substance powder and the film thickness from the fine powder; hence, it

can be optionally controlled according to the mixed amount and the mixing conditions of the core substance and fine powder. A microcapsule having an average particle size of 1 to 1,500 μm can be obtained satisfactorily. During this mixing and stirring operation, the wall substance powder is readily pulverized by the core substance, as mentioned above, at this stirring temperature; hence, while each of the core and wall substance collide with one another, the wall substance is pulverized and sticks physically to the surface of the core substance, the colliding surface of each substance is frictionally heated locally, and the viscosity of the wall substance becomes lower than that of the core substance; hence, the wall substance flows and becomes smeared on the surface of the core substance. As a result, the core substance powder is covered with the wall substance.

The microcapsule obtained by the above process becomes a pliable powder having good flowability even at room temperature, and the powder of the core substance is covered completely with the fine powder.

In addition, when the airtight effect of the core substance of the resulting microcapsule and the strength of the capsule need to be enhanced, the microcapsule obtained by the above process is covered further with a polymer film. That is, the powder of the core substance is covered with a relatively small amount of fine powder, after which it is covered with a polymer film in a conventional microencapsulation method. In this case, it is necessary to consider the affinity between the capsule and polymer film as well as the polymer film solution. Microencapsulation

with a water-soluble polymer is suitable for the microcapsule covered with a hydrophilic fine powder, and specifically, a coacervation method with gelatin or the like can be used. In addition, the microencapsulating method with a hydrophobic polymer, such as a coacervation method, from an organic solvent solution is suitable for a microcapsule covered with a hydrophobic fine powder.

Moreover, the shape-holding power of the microcapsule is far superior and the stability is better, the higher the viscosity of the core substance, and preferably one which can be thickened or gelled by preadding a filler, thickener, gelling agent, or the like thereto.

According to this kind of manufacture of a microcapsule, the core substance is frozen, ground, and pulverized, then mixed and stirred under a low temperature after adding the wall substance thereto; hence, the contamination of the core substance with the fine powder is reduced, and therefore, the core substance can be covered with a very small amount of fine powder efficiently, and a decline of the properties of the core substance of the microcapsule due to the fine powder is minimized. In the middle of the manufacture, there is no loss of the core substance and fine powder at all, and microencapsulation is possible at a 100% yield. A microcapsule can be manufactured in a simple step in a short length of time, and the manufacturing apparatus may just be a stirrer. As a consequence, the manufacturing cost is reduced remarkably. Moreover, all of the steps are performed under low temperatures; hence, an unstable core substance also can be microencapsulated without denaturing or

deteriorating the core substance and fine powder. Furthermore, as compared to a conventional method in which water or an organic solvent is used, a drying step and drainage treatment are unnecessary, so the work is much safer. Adjustment of the particle size of the microcapsule is performed optionally with ease; hence, a microcapsule having a particle size corresponding to the objective can be prepared with ease.

This will now be described specifically with reference to the practical examples.

[Practical Example 1]

Water colored by methylene blue was cooled and solidified, after which it was ground using a stirrer with a cutter to obtain a frozen powder having an average particle size of 50 μm , 100 weight parts of this powder was mixed and stirred with 5 weight parts hydrophobic silica fine powder (trade name: Aerosil R972 made by Nihon Aerosil Co.; average particle size: 16 μm) in a high-speed stirrer with a cutter while keeping it at -20°C , which was the temperature at which it did not agglomerate. Upon stirring this for 10 seconds at a stirring rate of 20,000 rpm, a microcapsule wherein the surface of a colored water powder was covered with a fine hydrophobic silica powder was obtained. Moreover, the temperature was -10°C when mixing and stirring are finished. This microcapsule was outstanding at fluidity even at room temperature in a pliable state. In addition, blue water was released from a microcapsule in which this microcapsule was spread over paper and then pressurized.

[Practical Example 2]

Upon manufacturing a microcapsule in entirely the same way as in as in Practical Example 1, a pliable powder outstanding in flowability even at room temperature was obtained with a commercially-available starchy paste (trade name: Yamato Paste) as the core substance. This microcapsule powder was spread on paper, and upon subsequently sticking another sheet of paper thereto and pressurizing and drying it, the two sheets of paper were adhered well.

[Practical Example 3]

Butter was cooled and frozen to -60°C with liquid nitrogen and ground using a stirrer with a cutter to obtain a frozen powder having a 50 μm average particle size. While keeping 100 weight parts of this powder at -50°C , which was the temperature at which it did not agglomerate, upon mixing and stirring it with 5 weight parts fine silica powder (trade name: Aerosil 200; average particle size: 16 μm) for 10 seconds at a stirring rate of 20,000 rpm using a stirrer with a cutter, a fine silica powder capsule of butter was obtained at a 100% yield. This was a pliable powder having good flowability even at room temperature.

[Practical Example 4]

A crosslinking and desolvating agent was obtained from an acrylate-based tacky adhesive (trade name: SK-Dyne 1504, made by Soken Chemical Co., Ltd.) until a sufficient adhesive power was produced. After freezing this with liquid nitrogen, a powder having an average particle size of 50 μm was obtained using a stirrer with a cutter. While keeping

100 weight parts of this powder at -60°C , which was the temperature at which it did not agglomerate, upon mixing and stirring this with 10 weight parts of a fine silica powder (trade name: Aerosil 200) using a stirrer with a cutter at a stirring rate of 20,000 rpm for 30 seconds, a fine silica powder capsule of a tacky adhesive was obtained,

[Practical Example 5]

10 g of the microcapsule powder obtained in Practical Example 4 was mixed with a 10% gum Arabic aqueous solution dispersed in 30 g of a 10% warm gelatin aqueous solution, 140 mL of 40°C water were further added under stirring, a 10% acetic acid solution was added dropwise, the pH was adjusted to 4.2, the above-mentioned powder was included by a coacervation drip. This dispersion was cooled further to 5°C , 1 mL of 30% formalin solution was added, then a 10% NaOH aqueous solution was added to adjust the pH to 9, then upon increasing the temperature to 50°C at a rising temperature rate of $1^{\circ}\text{C}/\text{min.}$, a double microcapsule wherein the surface of the above-mentioned microcapsule was covered with gelatin was obtained. Upon flow-drying this double capsule, a microcapsule powder having a good shape-holding power and flowability was obtained.

As described above, in the manufacture of a microcapsule of this invention, a core substance, which comprises a substance that becomes a liquid, agglomerates, or cannot keep its powdery form near room temperature, when obtained in powder form, is frozen and ground at a low temperature at which the powder thereof does not thaw or agglomerate, then this is mixed and stirred with a fine powder at this temperature; hence, a core

substance can be obtained from a liquid, a substance having tackiness, a soft substance, or a substance that is submersible in or reacts with water or an organic solvent, each near room temperature, and microcapsules can be obtained by [illegible] these core substances by an operation of simple steps in a short time and at a 100% yield. These microcapsules can be used in tacky adhesives, bonding agents and paints, as well as electrophotographic materials such as toners, drugs, and the like, with the range of applications being extremely wide. Moreover, in comparison to a conventional method, during manufacture, water or an organic solvent is not used at all; hence, the drying step or drainage treatment becomes unnecessary, making the industrial safety high as well. There are further advantages because microcapsules having any given particle size can be manufactured with ease, and diverse microcapsules can be obtained in accordance with the objective, and so forth.